Complex Shapes and Dynamics of Dissolving Drops of Dichloromethane**

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There is a growing interest in synthetic, chemical systems capable of undergoing autonomous shape changes and/or self-motion.[9] Important examples include solid objects such as catalytic Au/Pt nanorods,[2] mechanically responsive gels driven by oscillating reactions,[3,4] and liquid systems in which self-motion is induced by surface-tension gradients.[5–7] The latter class of systems includes iodine/iodide-containing oil droplets on glass surfaces under aqueous solutions of stearyltrimethylammonium chloride[8] as well as drop motion on an alkylsilane-treated silicon surface with spatial “wettability” changes.[9]

Droplet motion on air–water interfaces is usually driven by a Marangoni effect involving temperature or concentration gradients.[10] A typical example are pentanol droplets on water, which depending on the drop volume, perform erratic or unidirectional motion and also show very disorganized forms of droplet fission.[11] This fission can extend from the millimeter-scale down to nanoscopic micelles.[12]

Herein, we investigate the dynamics of water-saturated dichloromethane (CH$_2$Cl$_2$, 25 µL) droplets on aqueous solutions of cetyltrimethylammonium bromide (CTAB). Figure 1 is a qualitative phase diagram describing the macroscopic dynamics in the CH$_2$Cl$_2$/CTAB system at five different concentrations of the surfactant CTAB.

The typical life time of the dissolving droplets ranges between 20 and 90 s. The time axis is not to scale as the diagram emphasizes distinct, successive states in the drop evolution. Single arrows indicate rotation of the drop around its geometrical center. The double arrow indicates that the drop moves back and forth along a fixed line. The field of view of all frames corresponds to 13 x 13 mm$^2$.

Figure 1. Qualitative description of the drop evolution in the CH$_2$Cl$_2$/CTAB system at five different concentrations of the surfactant CTAB. The typical life time of the dissolving droplets ranges between 20 and 90 s. The time axis is not to scale as the diagram emphasizes distinct, successive states in the drop evolution. Single arrows indicate rotation of the drop around its geometrical center. The double arrow indicates that the drop moves back and forth along a fixed line. The field of view of all frames corresponds to 13 x 13 mm$^2$.

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commence with the aforementioned lateral oscillations and then give way to drop rotation. The rotating drops eject droplets that form patterns reminiscent of Fibonacci spirals. For $1 \text{mmolL}^{-1}$ (third column), the initial drop pulsates periodically and its edge is well described by concentric circles of oscillating radius. During this beating motion, the surrounding film spreads periodically and rather violently over larger distances (see also Figure 2 a–d). Close to its maximal extension, the edge of the film breaks into a halo of typically 20–30 droplets and, while recoiling, produces patterns reminiscent of dewetting structures. The period of these phase-locked processes is 0.6–1 s. The drop then transforms into an elongated structure with two sharp tips. This structure rotates in an arbitrary but usually constant direction. Later additional tips form and create asymmetric drop shapes that often transform into rotating drops with three or sometimes four tips. We observe similar structures also at $[\text{CTAB}] = 10 \text{mmolL}^{-1}$ (fourth column). However, pulsating drops are absent and rotation dominates this intermediate concentration range.

For the highest concentration in Figure 1, dichloromethane drops show neither pulsation nor rotation but have a polygonal rim featuring several small tips. These tips move erratically along the drop boundary and mediate changes in its shape (Figure 2 e, f). Emission of a single droplet from a non-rotating polygonal drop at $[\text{CTAB}] = 30 \text{mmolL}^{-1}$. The tip-shaped deformations move along the drop’s boundary, collide (e), and eject one droplet in an upward direction (f). The photos in (e) and (f) are transmission micrographs of the backlit sample. Field of view and time between frames: $20 \times 20 \text{mm}^2$, 67 ms (a–d) and $15 \times 19 \text{mm}^2$, 111 ms (e, f).

Figure 3 a–d) Image sequence of a rotating, two-armed dichloromethane drop at $[\text{CTAB}] = 6.8 \text{mmolL}^{-1}$. Time between frames is 210 ms. Field of view: $9 \times 9 \text{mm}^2$. e) Rotational angle of a similar drop as a function of time and its linear least-square fit (gray line). The inset shows a 21 s-long trajectory of the drop’s geometrical center. Scaling bar: 1 mm. f) Snapshot of a rotating two-armed drop at $[\text{CTAB}] = 6.8 \text{mmolL}^{-1}$. Superposed are the trajectories of daughter droplets (dark dots) ejected directly by the mother drop and third generation droplets (bright dots) created during the fission of second-generation droplets. Analyzed time interval: 770 ms. Field of view: $17 \times 17 \text{mm}^2$.

In our experiments the rotating two-armed drop is the most frequently encountered and longest lasting structure. For $[\text{CTAB}] = 1 \text{mmolL}^{-1}$, the initial drop pulsates periodically and its edge is well described by concentric circles of oscillating radius. During this beating motion, the surrounding film spreads periodically and rather violently over larger distances (see also Figure 2 a–d). Close to its maximal extension, the edge of the film breaks into a halo of typically 20–30 droplets and, while recoiling, produces patterns reminiscent of dewetting structures. The period of these phase-locked processes is 0.6–1 s. The drop then transforms into an elongated structure with two sharp tips. This structure rotates in an arbitrary but usually constant direction. Later additional tips form and create asymmetric drop shapes that often transform into rotating drops with three or sometimes four tips. We observe similar structures also at $[\text{CTAB}] = 10 \text{mmolL}^{-1}$ (fourth column). However, pulsating drops are absent and rotation dominates this intermediate concentration range.

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droplets (bright dots in Figure 3f), which sometimes split into a fourth (detectable) generation. Notice that the second-generation droplets are ejected in radial direction. Therefore droplet ejection neither drives nor contributes to the generation of rotational motion.

The combination of evaporation, solubilization, and surfactant transfer in the CH₂Cl₂/CTAB system makes it highly susceptible to surface-tension-driven thermal and solutal Marangoni instabilities. In this context, the transitions between the distinct drop shapes are closely related to the formation of the surrounding film and its horizontal area. The film is controlled by the spreading power of CH₂Cl₂, which decreases with increasing concentrations of both CTAB and CH₂Cl₂. Accordingly, thermal effects are favored at low surfactant concentrations and hence are the likely cause of the lateral and concentric drop oscillations as well as of the associated droplet patterns. For qualitatively similar wetting conditions, Marangoni-driven spreading is also known to induce self-propulsion of aniline drops. Their motion is initiated by an, induced or fortuitous, asymmetry of the spreading film. The resulting imbalance in surface tension is further amplified and sustained by the dissolution of the film in the wake of the moving drop. The same mechanism might explain the laterally oscillating and circling motion patterns in our experiments. However, it clearly fails to account for the observed changes in the film size and the formation of the small droplet patterns.

At higher CTAB concentrations the spreading power of CH₂Cl₂ is low and the drops are more compact. Under such conditions, the solutal Marangoni instability is expected to dominate the system and hence should be a major factor in the observed drop rotation. This interpretation is further supported by our observation of a pair of convection cells at intermediate CTAB concentrations (see Figure S1 in the supporting information). These cells occupy roughly equal halves of the drop, organize fluid motion at the air/water interface, and are not seen at low concentration. Their faint optical contrast is due to spontaneous emulsification which is rather typical at water-oil interfaces subjected to surfactant transfer.

In summary, we have shown that dichloromethane drops floating on an aqueous CTAB solution can evolve into a surprising range of shapes and motion patterns. The underlying mode selection is very sensitive to the experimental conditions including the concentration of CH₂Cl₂ in the aqueous and gas phase. Despite this limitation, we have identified distinct and novel dynamic states such as symmetrical pulsating drops, multi-armed rotors, and polygonal drops. These shapes are sufficiently stable to undergo dozens of rotation and pulsation cycles or, in the case of the polygonal drops, entertain intricate dynamics of their tips. Coupled to these shape-forming processes is the emission of very small but macroscopic droplets. The droplets can describe linear trajectories and split in a cascading fashion. While linear drop motion had been reported in other systems involving the Marangoni effect, this well-organized cascading decay is an additional novelty. These surprising findings in a seemingly simple system must be related to the specific choice of chemical species. In contrast to many other poorly water-soluble organic solvents, CH₂Cl₂ has a very low boiling point and a high density. Furthermore, we observed similar phenomena in experiments employing the surfactant C₆H₄TAB but not for (the nonionic) Brij35.

Experimental Section

All chemicals used are of analytical grade. Cetyltrimethylammonium bromide (CTAB; Aldrich, > 99 %) and dichloromethane (Aldrich, HPLC grade) were used as purchased. The water is ultra-pure (resistivity > 17 MΩcm). All experiments are carried out at room temperature. The CTAB solution (25 mL) is filled into a cylindrical container (diameter 70 mm) and a single 25 µL drop of CH₂Cl₂ is carefully placed onto the solution surface using a pipette. The system is then covered by a glass plate to reduce matter exchange between the gas layer above the fluid and the surroundings. It is illuminated with white light and the shadow of the floating, lens-shaped drop is monitored from the top with a video camera. Note that the densities of CH₂Cl₂ (1.33 g mL⁻¹) and water-saturated CH₂Cl₂ are larger than the density of water. The solubility of dichloromethane in water is 13 g L⁻¹, which corresponds to a volume 250 µL in 25 mL. The reproducibility of the experiment is greatly increased by saturating the organic liquid dichloromethane with water. This procedure is used for all experiments and data presented in this study. The solubility of water in CH₂Cl₂ is 2 g L⁻¹ at 25°C. The solubility of CH₂Cl₂ in water is 13 g L⁻¹ (153 mmol L⁻¹), which corresponds to a total volume of 0.25 mL in 25 mL of water and, hence, the equivalent of ten of our dichloromethane drops. The solubility of CTAB in water is 15 g L⁻¹ (41 mmol L⁻¹). The partitioning of CTAB between the aqueous and the CH₂Cl₂ phase highly favors the organic liquid. The critical micellar concentration of CTAB in pure water is 0.8 mmol L⁻¹ (γₘₐₓ = 30.2 mN m⁻¹). However, in the presence of CH₂Cl₂, an oil-in-water microemulsion is formed and the critical aggregation concentration is decreased to 0.1 mmol L⁻¹ (γₘₐₓ = 61.5 mN m⁻¹; γₜₙ = 1 mN m⁻¹). The microemulsion also affects the solubility and solubilization kinetics of CH₂Cl₂ in water.

A typical set of experiments involved five different concentrations of CTAB. For each concentration, the dynamics of five successive droplets were studied. We reproduced these sets of 25 experimental runs several times and on different days. The general succession of patterns is always maintained. The data in Figure 1 are obtained from the fourth or fifth repeat runs. Results obtained at both lower and higher concentration limits have the highest reproducibility.

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